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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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INVENTOR(S)

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TITLE OF THE INVENTION (500 characters max)

CHEMILUMINESCENT PAINT PROJECTILES AND METHOD OF PREPARATION

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60/513088
102103

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ENCLOSED APPLICATION PARTS *(check all that apply)*

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☐ Application Date Sheet. See 37 CFR 1.76

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METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☒ Applicant claims small entity status. See 37 CFR 1.27.

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Respectfully submitted,

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Date October 21, 2003

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TITLE

[0001] CHEMILUMINESCENT PAINT PROJECTILES AND METHOD OF PREPARATION

BACKGROUND

[0002] There has been work in the area of projectile markers and projectiles filled with paint materials.

DETAILED DESCRIPTION

[0003] The method of marking a target with a paint filled projectile fired from a projectile launching device has been practiced for many years. Initially a soft gelatin capsule was filled with an oil-based paint and the resulting projectile was used to mark trees for felling during lumbering operations. As other applications developed and the target marking practice expanded, people began shooting each other. Out of these initial semi-hostile encounters, a rapidly growing sport known as "paint ball" or "paint balling" has evolved. The sport is characterized by numerous game formats from simple indoor target shooting to wide ranging war games involving multiple teams of participants deployed over relatively large expanses of natural terrain. Organized paint ball groups and organizations now sponsor local, national and international paint ball competitions. In addition, the practice of paint ball is also widely adapted and used in police and military training exercises. Whether for recreational or vocational training, paint ball activities are conducted increasingly in low light conditions such as outdoor nighttime exercises and within indoor facilities in both daytime and nighttime settings. Marking a target during the reduced lighting conditions is highly desirable.

[0004] The widespread popularity of paint balling has created a growing demand for increasingly sophisticated launch devices known as markers as well as projectiles with improved ballistics, marking capability, and performance. The projectile launching devices have evolved to an astonishing degree to

produce futuristic designs capable of rapid fire with amazing range and accuracy. Projectiles have also evolved but have hardly kept pace with the increasing demands of the sport and its highly developed launching devices and protective equipment.

[0005] The projectile or paint ball consists of a plasticized frangible outer capsule that forms an interior chamber containing the marking composition or paint. A properly designed and manufactured projectile is capable of being launched without breakage and yet is capable of fragmentation upon impact with the target without causing serious harm or damage to the target.

[0006] Initially, modified pharmaceutical gelatin compositions were filled with commonly available oil based paints using standard manufacturing equipment and practices common to the pharmaceutical industry for the manufacture of soft gel caps. As discussed in U.S. Patent No. 3,861,943, water-washable projectile filling compositions were described. Rouffer, in U.S. Patent No. 5,393,054, discloses the use of polysorbates combined with colored pigments, a suspending agent and an antifoam agent to produce a water-washable filler composition.

[0007] The importance of component compatibility with standard plasticized soft gelatin encapsulating compositions was recognized and addressed by selecting filler components which were compatible with commonly used gelatin compositions. Haman and Schmoke, in U.S. Patent No. 4,656,092, disclose the use of FD&C coloring agents along with titanium dioxide white pigment and fumed silica in a vegetable oil-vegetable shortening matrix also enclosed in a standard soft elastic gelatin capsule composition.

[0008] The use of colored, water washable polyethylene glycol (PEG) based filler compositions soon developed and the ZAP Paintball Company commercialized an improved PEG-starch filler composition enclosed in a starch containing gelatin capsule (See U.S. Patent No. 5,393,054). Christy L. Olson, in U.S. Patent Nos. 5,353,712 and 5,448,951 discloses the use of

thermoplastic injection molded starch compositions manufactured by a method described in U.S. Patent No. 4,738,724 for the production of improved projectiles suitable for use in compressed gas operated launchers such as paint ball markers. Olsen discloses the use "of any non-toxic non-water based liquid capable of carrying a washable bright dye. . ." failing to recognize the importance of filler component compatibility with the capsule compositions. Kotsiopoulos and Gibson in U.S. Patent No. 5,639,526 disclose the use of injection molded thermoplastic linear polymers such as polystyrene in the construction of projectiles impervious to water and suitable for containing fill materials incompatible with the commonly used gelatin compositions. While a polystyrene constructed enclosure would accommodate water based fill compositions and would be resistant to environmental attack by oxygen, water, heat and light, it would not be compatible with many petrochemical based compositions containing hydrocarbons, ketones, esters, ethers and other components which are incompatible in polystyrene containers. Bayless, Loba and Reynolds, in U.S. Patent No. 5,885,671, disclose lowered freezing point plasticized gelatin capsule fill compositions based on polyethylene glycols, water, oleaginous materials such as mineral oil, cross linking monomers which impart stability to the gel, partially neutralized carboxylic copolymers and ethoxylated glycerides in combination with titanium dioxide pigment and water soluble FD&C dyes as colorants. The fill compositions are loaded into plastic gelatin encapsulating materials using established manufacturing procedures.

[0009] The a luminescent paint ball projectile for marking night time target impacts was introduced by Henry J. Smith (see U.S. Patent Nos. 5,001,880 and 5,018,450). The subject projectiles of those disclosures were based on unspecified encapsulating materials formed and filled in a double fused hemisphere arrangement. The subject projectiles were not amenable to production using standard paint ball manufacturing machinery but rather required special tooling and encapsulating equipment. The two hemispheres were filled with oxalate ester components, one hemisphere being filled with a

hydroperoxide solution plus fluorescent compound and the other with the oxalate ester fuel composition. The peroxyoxalate ester components, particularly the negatively substituted oxalate esters are incompatible with many of the commonly used encapsulating components leading to poor product shelf life.

[0010] Robeson in U.S. Patent No. 5,967,916 describes luminescent projectiles. The proffered virtue of the improved projectiles is low impact damage, reusability and nighttime trajectory tracking similar to the tracer bullet. The system utilizes fluorescent dyes or a phosphorescent composition that glows when illuminated with incident black light radiation. The system requires background black light illumination and leaves no visible mark on the impacted target. Although this system has been used, it lacks many of the features that make paint ball contests fun and exciting. The sport also requires background black light illumination and is therefore limited to spaces defined by an existent field of black light illumination.

[0011] Still another luminescent target marking system incorporates phosphorescent pigments with other commonly used fillers contained in standard frangible projectiles. See U. S. Patent Nos. 6,082,349 and 6,298,841 B1. The proffered advantage of this system is the manufacture and filling of paint ball projectiles using standard manufacturing equipment common to the industry. However, phosphorescence is a relatively short lived, inefficient process which requires charging by exposure to bright light prior to use. The charge up process requires either special charging equipment, which is retrofitted to existing guns, or special charging equipment independent of the gun, where the balls may be separately charged prior to use. Such charges require a power source and when retro fitted to existing guns, prove inconvenient and unwieldy in use. Incorporating different phosphors with other dyes and pigments gives light outputs of different colors. Once the projectiles are charged however, the light emission is fixed by the natural decay curve of the inherent phosphorescence process. The light emission is bright immediately

after charging, but becomes relatively dim with the passage of time. The time of emission is also fixed by the inherent decay process. Decay times are typically measured in many minutes to hours, depending on the level of charge.

[0012] A good light emitting paint ball should be economical to manufacture using standard encapsulating equipment commonly available to the industry. The projectiles should not be too brittle or too soft and should be usable in existing paint ball markers without modification. The marking material should be clearly visible on impact for several seconds to minutes and should possess the other desirable properties generally expected with fillers commonly used in the industry, i. e. washability, target surface adhesion, low splatter radius, and good marking properties. In addition, the luminescent projectiles should have good ballistic properties, good shelf life, and should produce a luminescent mark which is clearly visible for several minutes under low light as well as dark conditions.

[0013] Auto oxidation (autoxidation) is the oxidation of a substance by its direct combination at ambient temperatures with oxygen, usually from air exposure. Autoxidation is a widely investigated phenomenon and frequently the subject of many studies. Many of these studies relate to the prevention of autoxidation in food and other consumer products with antioxidants. Chemiluminescence is the production of light through a chemical reaction. Autoxidation is frequently accompanied by chemiluminescence although in most instances, the light emission is not sufficiently bright to be of any practical utility. Although comparatively rare, bright autoxidative chemiluminescence can be very desirable.

[0014] Cutler, Carlon and Sherman U.S. Patent No. 3,515,070 disclose the use of brittle gelatin capsules up to 3/16 inch diameter for filling various munitions. They also disclose the potential for soft gelatin encapsulation similar to the type used in preparing pharmaceutical products where wall thickness is at

least 7.5 mils. Specific soft gelatin compositions that are compatible with peraminoethylenes are not disclosed and wall thickness of 20 to 30 mils is generally required for projectiles suitable for use in compressed gas powered guns such as paint ball markers. Marcus and Gloye U.S. Patent No. 3,973,466 found that pharmaceutical soft gelatin capsules were not suitable to provide environmental protection or the desired frangibility to suit their purposes. Narcus and Gloye disclose the use of non-gelatin encapsulation systems. These systems, however, would be entirely unsuited for use as projectiles in compressed gas powered paint ball markers because of their designed frangibility, non uniform size and non-spherical shapes.

[0015] DEFINITIONS

[0016] "Paint ball" is a term used to describe a game played by numerous game formats from simple indoor target shooting to wide ranging war games involving multiple teams of participants deployed over relatively large expanses of natural terrain or sometimes paint ball is used to describe the round or semi round projectile used in the game of paint ball.

[0017] "Luminescence" is a phenomenon which occurs when energy is produced in the form of visible light. Luminescence may be represented as follows:

[0018] $A + B \rightarrow X^{*} + Y$

[0019] $X^{*} \rightarrow X + hv$

[0020] Where X^{*} is an electronically excited molecule and hv represents light emission upon return of X^{*} to a lower energy state.

[0021] "Chemiluminescence" is a phenomenon which occurs when one or more chemicals react in a way that produces energy at or near ambient temperatures in the form of visible light. This visible light is usually more visible in the dark. This form of light production is sometimes referred to as "cold light."

[0022] "Autoxidation" or "auto oxidation" is the oxidation of a substance by its direct combination at ambient temperatures with oxygen, usually from air exposure.

[0023] "Projectile" is an article launched toward an intended target that leaves a visible mark on the target. In the sport of "paint ball", the projectile is sometimes referred to as a paint ball.

[0024] "Marker" or "projectile launching devices" are used in paint ball games or other applications to launch projectiles at an intended target. A typical projectile will be launched with a compressed gas paint ball gun, or blowgun.

[0025] "Component" is a material or chemical that is used in the preparation or manufacture of a projectile.

[0026] "Fill composition" or "fill material" is the liquid, solid or liquid-solid suspension that is used on the interior of a paint ball. An outer shell to keep its contents from leaking usually surrounds the fill composition or material.

[0027] "Shell material" is the frangible outer shell of a paint ball. The shell is usually constructed from a polymeric material such as gelatin, or polyvinyl alcohol in such a way to maintain a hard outer surface, which is frangible enough to burst open on contact with a hard surface after being launched by a projectile launch device.

[0028] This disclosure relates to luminescent projectiles based on chemiluminescent autoxidation systems suitable for use with projectile launchers such as compressed gas powered guns to fire paint balls.

[0029] There are a number of significant problems that must be simultaneously addressed in order to construct a single compartment chemiluminescent projectile suitable for use in compressed gas operated launching devices such as paint ball markers. First, it must be recognized that chemiluminescent systems generally require an oxidant, which reacts with a fuel to generate a substantial population of first singlet excited state emitters.

Generally, the fuel component must be maintained separately out of contact with the oxidant until the light is desired. When the light is desired, the fuel is mixed with the oxidant and light is produced. It must be recognized that air is about 20 percent oxygen and that oxygen is capable of acting as oxidant in autoxidative chemiluminescent systems. The process is referred to as chemiluminescent autoxidation and is quite common but light outputs are generally not of any practical utility. Single compartment chemiluminescent projectiles require a relatively efficient chemiluminescent autoxidation process with defined light outputs in the range of 1 to $1x10^{-5}$ Einsteins per mole, preferably 1 to $1x10^{-3}$ Einsteins per mole to be usable. The first consideration then is to identify suitable chemiluminescent autoxidation processes meeting these minimum requirements.

[0030] Second, it must be recognized that chemiluminescent autoxidation systems are sensitive to a number of substances that reduce or quench light outputs to the point where the light output is of no utility. Quenchers and inhibitors may be acids, bases, oxidizable or reducible transition metals, salts, water, oxygen, common solvents and polymers. Each chemiluminescent autoxidation system will have its own unique set of compatibility requirements, which will limit capsule filling formulations. It must be appreciated that a selected chemiluminescent autoxidation system must be combined with appropriate non-reactive compatible ingredients, which produce a suitable target marking composition.

[0031] Third, the fill composition, including the chemiluminescent autoxidation system, must be compatible with all of the ingredients used in the encapsulation system. The interior walls of the capsule forming the projectile must not react with or be incompatible with the fill material.

[0032] Fourth, the outer capsule wall of the projectile must be compatible with conditions and elements found in the environment such as heat, light, oxygen, water, and reasonable impacts. The capsule must be capable of

protecting its contents from the effects of these forces and elements, particularly, exposure to oxygen. The finished capsule must be suitable for use in projectile launchers such as compressed gas operated projectile launchers to fire paint balls. The capsules must also possess the characteristics and qualities that have been found desirable in commonly used projectiles such as paint balls. The finished paint ball must be sufficiently tough to withstand normal handling and firing from the launch device without breakage but must be frangible enough to break on impact with the target without causing undue damage to the target. The projectiles must not swell or otherwise deform on exposure to environmental conditions and must have favorable ballistics. The fill material should leave a uniform impact pattern of 2 to 5 inches in diameter, which adheres to the target surface without undue running. The marking material should be water washable, safe, non-toxic, and environmentally harmless.

[0033] Surprisingly, it is possible to simultaneously satisfy all of the aforementioned requirements to produce a single compartment luminescent projectile suitable for use in compressed gas operated guns such as paint ball markers. The simultaneous satisfaction of these requirements depends on the careful testing and evaluation of component compatibilities and the careful selection of ingredients that satisfy all of the requirements for a suitable projectile.

[0034] Single compartment autoxidation systems have a number of advantages over other luminescent projectile systems. The single component systems do not require specially constructed multi-compartment capsules or special manufacturing equipment. Projectiles can be manufactured by simply substituting the chemiluminescent fill material for the standard fill material in an existing production line. Autoxidation chemiluminescent projectiles do not require black light background lighting and can be used in wide ranging outdoor pursuit activities. Chemiluminescent projectiles can be used without

charging prior to use and without expensive and cumbersome retrofit attachments on existing compressed gas driven projectile launchers.

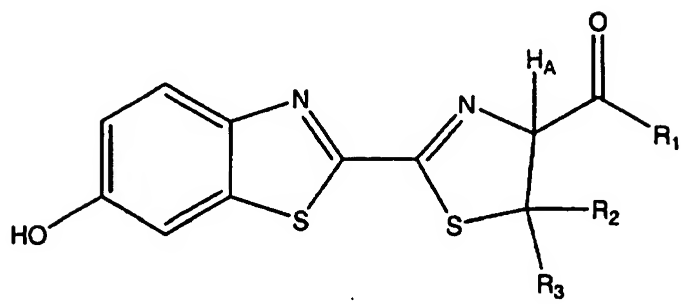
[0035] The autoxidation chemiluminescent luminescent projectiles, which are the subject of this invention, can utilize filler materials and compositions already known in the art provided that the compositions do not contain materials that seriously quench the light output or are otherwise incompatible with the autoxidation components. Standard encapsulating materials may also be used so long as they are not incompatible with other system components. It should be noted however, that each autoxidation system would have its own unique set of compatibility requirements that in some instances greatly limit the choice of fill formulations and other system components.

[0036] Paint balls described herein involve production of an air activated luminescent projectile suitable for use as a paint ball with projectile launching devices. We have found that by selecting a suitable luminescent autoxidation system, which produces adequate light under the conditions of use and combining this system with suitable projectile filling compositions housed in a compatible encapsulating material, we have formed just such a luminescent projectile.

[0037] In principle, any luminescent autoxidation system satisfying the minimum light output requirements of 1 to $1x10^{-5}$ Einsteins per mole, preferably 1 to $1x10^{-3}$ Einsteins per mole with adequate air reactivity to release its light capacity in seconds to a few hours, could be used. The following compounds may satisfy these requirements:

[0038] Formula I:

I: Benzothiazoles related to firefly luciferin



I

[0039]

[0040] R_1 may be a leaving group which in its protonated form has an acid constant (pKa) of $1x10^{-9}$ or higher, preferably $1x10^{-6}$ or higher. Several such leaving groups are known in the art and by way of illustration may include phosphate, phenol, thiophenol, aryl esters, and various heterocycles. R_1 may not be aliphatic esters.

[0041] When R_1 is hydroxy and functionalized by enzymatic phosphorylation with adenosine triphosphate, enzymatically catalyzed oxidation reactions yield higher light outputs than simple base catalyzed reactions with oxygen.

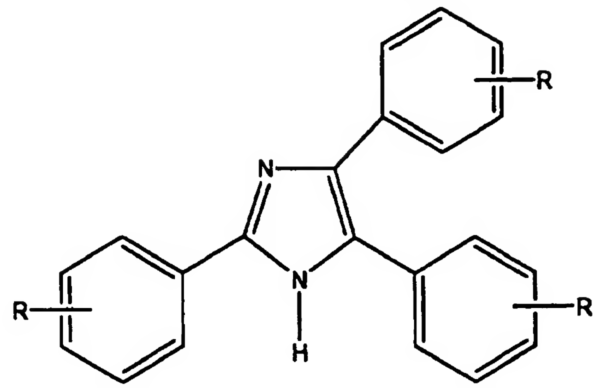
[0042] R_2 may be H, and C_1-C_{12} hydrocarbon including linear, branched, or cyclic hydrocarbon, aryl, benzyl, unsaturated hydrocarbon, alkoxyl, or halgoen but halogen does not include iodine.

[0043] R_3 may be H, and C_1-C_{12} hydrocarbon including linear, branched, or cyclic hydrocarbon, aryl, benzyl, unsaturated hydrocarbon, alkoxyl, or halgoen but halogen does not include iodine.

[0044] The benzothiazoles (Formula I) related to firefly luciferin are operable with or without firefly luciferase depending upon the substitution pattern of R_2 and R_3.

[0045] Formula II:

II. 2,4,5-Triarylimidazoles related to lophine

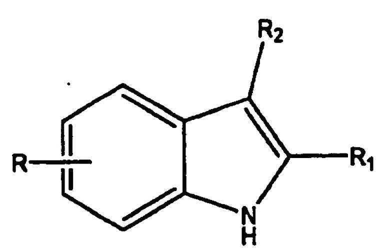


II

[0046] R may be H, C_1-C_{12} alkyl including linear, branched, or cyclic alkyl, C_1-C_{12} alkoxyl including linear, branched, or cyclic alkoxyl, cyano, C_1-C_{12} carboxy esters, C_1-C_{12} ketones, or halogen except that halogen does not include iodine. The R groups may be the same or different. R cannot be nitro.

[0047] Formula III:

III. Indoles



III

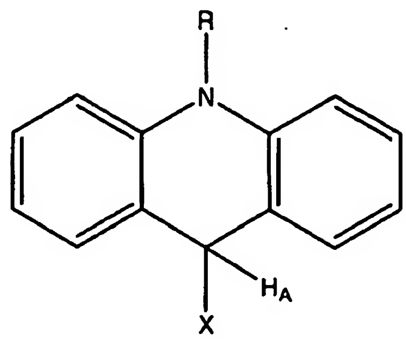
[0048] R_1 may be H, C_1-C_{12} alkyl including linear, branched, or cyclic alkyl or aryl.

[0049] R_2 may be H, C_1-C_{12} alkyl including linear, branched, or cyclic alkyl or aryl.

[0050] R may be H, C_1-C_{12} alkyl including linear, branched, or cyclic alkyl, aryl, C_1-C_{12} alkoxy, or halogen but halogen may not be iodine. R cannot be nitro.

[0051] Formula IV:

IV: N-Substituted acridan nitriles and carboxylate esters



IV

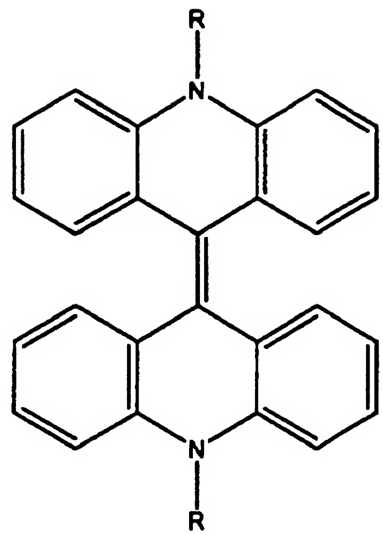
[0052]

[0053] R may be H, aryl, C_1-C_{12} alkyl including linear, branched, or cyclic alkyl.

[0054] X may be cyano or ester of the formula –COZ where Z may be a leaving group which in its protonated form has an acid constant (pKa) of $1x10^{-9}$ or higher, preferably $1x10^{-6}$ or higher. Several such leaving groups are known in the art and by way of illustration may include phosphate, phenol, thiophenol, aryl esters, and various heterocycles. R_1 may not be aliphatic esters.

[0055] Formula V:

V. Biacridene



V

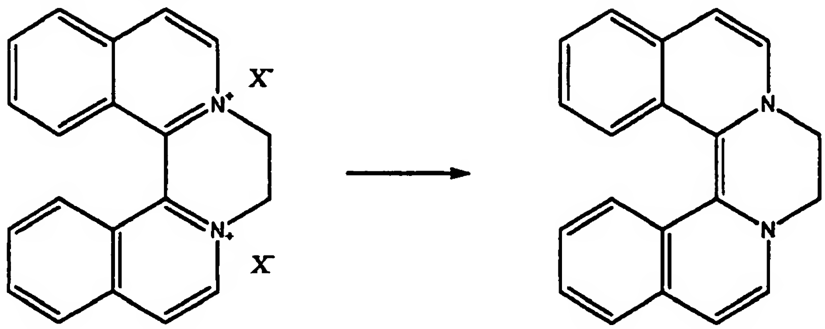
[0056] R may be H, C_1-C_{12} alkyl including linear, branched, cyclic alkyl, or aryl.

[0057] Formula VI: 1,1'-Bisisoquinolinium quatemary salts, and

[0058] Formula VII: Reaction products of 1,1'-Bisisoquinolium quaternary salts with base.

VI. 1,1'-Bisisoquinolinium quaternary salts, and

VII. Their reaction products with base

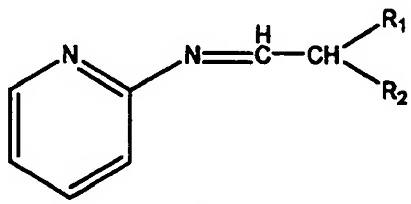


VI VII

[0059] X may be F, Br, or Cl. X may also be an anionic salt such as nitrate, citrate, sulfate.

[0060] Formula VIII:

VIII. 2-Aminopyridine Schiff bases



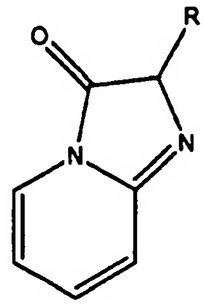
VIII

[0061] R_1 may be H, C_1-C_{12} alkyl including linear, branched, cyclic alkyl, or aryl.

[0062] R_2 may be H, C_1-C_{12} alkyl including linear, branched, cyclic alkyl, or aryl.

[0063] Formula IX:

IX. Imidazo[1,2-a]pyridine-3(2H)-ones

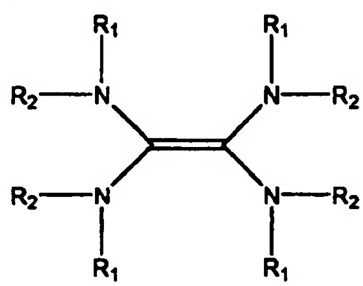


IX

[0064] R may be H, C_1-C_{12} alkyl including linear, branched, cyclic alkyl, or aryl.

[0065] Formula X:

X. Tetrakis(dialkylamino)ethylenes



X

[0066] R_1 may be C_1-C_{12} alkyl including linear, branched, or cyclic alkyl.

[0067] R_2 may be C_1-C_{12} alkyl including linear, branched, or cyclic alkyl.

[0068] R_1 and R_2 may also be a part of a unitary ring system extending from the same nitrogen atom such as $-(CH_2)_4-$, or $-(CH_2)_5-$.

[0069] R_1 and R_2 may also be a part of a unitary ring system extending from different nitrogen atoms (but those nitrogen atoms will be *ipso* to a common carbon) such as $-(CH_2)_2-$, or $-(CH_2)_3-$.

[0070] As can be seen from the above listed classes of compounds, a variety of compounds are available to serve as luminescent autoxidation substrates.

[0071] In some of the systems using the compounds selected from the group of Formulas I – X, strong base may be required to give rise to a triplet oxygen reactive carbanion. With respect to tetrakis(dialkylamino)ethylenes, no added base is required and the chemiluminescent agent spontaneously reacts with triplet oxygen.

[0072] In all of the different Formulas aforementioned, it is contemplated that only those functional groups designated by R, X, or Z that do not interfere with the luminescence property be utilized in the projectiles.

[0073] In practice, a chemiluminescent composition suitable for autoxidation is prepared by dissolving or dispersing one or more of the compounds selected from the group of Formula I – X in an appropriate carrier, the combination being called a fill material. Many fill materials may include other ingredients compatible with one or more of the chemiluminescent autoxidation systems described above. Carrier for the chemiluminescent agents may include:

[0074] (1) a solvent, such as mineral oil, polyethylene glycol, silicone oil, vegetable oil, or the like, which allows dissolution and or dispersion of the luminescent agent and other ingredients;

[0075] (2) a thickening agent, such as candelilla wax, paraffin wax, virgin paraffin wax, petrolatum, polysorbitol, or the like, which provides the bulk needed for the projectile and the ability to maintain solids suspension; and,

[0076] (3) and, a pigment, such as alumina, barium oxide, iron oxide, silica, titanium dioxide, zinc oxide, or the like, which provides a clearly visible spot. Many pigments are known to one skilled in the art and many of which could augment the illustrative list.

[0077] Aside from the carrier, the fill material may be supplemented with one or more of the following ingredients depending on the specific luminescent agent or the desired property:

[0078] (4) an activator, such as iso-butanol, t-butanol, ethylene glycol, ethylhexanol, noctanol, iso-octanol, n-decanol, n-hexadecanol, or the like, which enhances light output of the luminescent agent;

[0079] (5) a surfactant, such as Rhodacal™ reagents, Rhodasurf™ reagents, stearic acid, Tween™ reagents, or the like, which allows convenience in washing the fill material from an impact site after it has been used as a paint ball or to improve solubility and dispersion properties;

[0080] (6) a solids suspending agent, such as starch, cellulose, fumed silica, talc, or the like, which allows for the pigment and other solids to maintain suspension in the fill material;

[0081] (7) a dye, such as FD&C yellow, blue, or red, phthalocyanine green, or phthalocyanine blue, or the like, which allows for the pigment and other solids to maintain suspension in the fill material;

[0082] (8) a preservative or stabilizing agent, such as calcium chloride, calcium sulfate, lithium aluminum hydride, lithium bromide, lithium chloride, magnesium sulfate, sodium borohydride, sodium sulfate, or the like which enhances long term stability of the fill material, other electron rich additives such as vitamins and antioxidants; and

[0083] (9) a fragrance such as peppermint, spearmint which can act as an indicator to the target that he or she has been struck. The fragrance may dually serve to mask undesirable odors inherently present in the filler material before or after autoxidation.

[0084] Projectiles made with a carrier and other optional filler materials may also be encapsulated within a plasticized frangible outer capsule to provide a hard

outer wall. The outer wall protects its contents from oxygen and other elements or forces. Many encapsulating materials have been found to be compatible with one or more of the described chemiluminescent autoxidation systems. One encapsulating material comprises gelatin, hydrocarbon polymer, such as polyacrylate, polyethylene, polystyrene, polyvinyl alcohol, or the like, water, and one or more plasticizers, such as diethylene glycol, glucose, glycerine, mineral oil, parabens, starch, polyglycerol, sorbitol, or the like, added to create the appropriate shape, durability for firing from a projectile launcher and frangibility needed to break on impact with the target.

[0085] Preparation of the projectiles should be done in an oxygen-free atmosphere so as to preserve the chemical capacity of the chemiluminescent agent.

[0086] The selection of the chemiluminescent agent and/or dye, or pigment may also be used in a game or exercise to identify an individual or team. Each individual or team may be supplied with chemiluminescent paint balls containing distinctive non-chemiluminescent materials to distinguish individuals or team members. Such non-chemiluminescent materials include pigments such as alumina, barium oxide, iron oxide, silica, titanium dioxide, zinc oxide. The respective color can then be used to identify the source of hits by the corresponding person or team. In addition, each individual or team may be supplied with chemiluminescent paint balls containing distinctive chemiluminescent materials to distinguish individuals or team members. The respective color can then be used to identify the source of hits by the marker.

[0087] Another feature of using the chemiluminescent agents in a single-chamber shell inures from a stealth feature afforded to the person firing the projectile. Because the chemiluminescent reagents do not react until the shell is compromised by impacting on a target, the location of the person firing the marker remains uncertain. There is no tracer associated with the paint ball

as it travels between the marker and the impact site. This allows the person firing the marker to remain undetected.

[0088] EXAMPLES

[0089] These examples are in no way intended as limiting and serve only to illustrate a variety of compounds, carriers, fill materials and capsules, which are available. There are certainly a variety of additional compounds, which could serve equally well.

[0090] Examples of Oxidative Luminescent Compounds

[0091] Example 1

[0092] Tetrakis(dimethylamino)ethylene (Formula X, where R_1 and R_2 = $-CH_3$) can be prepared as described in US Patent 3,824,289 by reacting excess chlorotrifluoroethylene and dimethylamine under pressure. Product is isolated after extraction with aqueous alkali and water removal. Product is luminescent on exposure to air.

[0093] Example 2

[0094] Tetrakis(pyrrolidinyl)ethylene (Formula X, where R_1 and R_2 = $-(CH_2)_4-$) was prepared by combining 6 parts of dimethylformamide dimethyl acetal with 7 parts of pyrrolidine and heated to 110 °C as by-products were collected by distillation. After about 4 hours, the mixture was heated to 200 °C for about 2 hours as by-products were collected by distillation. The mixture was cooled and solid product was collected from acetonitrile. Product was luminescent on exposure to air.

[0095] Example 3

[0096] Tetrakis(piperidinyl)ethylene (Formula X, where R_1 and R_2 = $-(CH_2)_5-$) was prepared by combining 3 parts of dimethylformamide dimethyl acetal with 4 parts of piperidine and heated to 110 °C as by-products were collected by

distillation. After about 4 hours, the mixture was heated to 200 °C for about 2 hours as by-products were collected by distillation. The mixture was cooled and solid product was collected from acetonitrile.

[0097] Example 4

[0098] Tetrakis(morpholinyl)ethylene (Formula X, where R_1 and R_2 = -$(CH_2)_2O(CH_2)_2$-) was prepared by combining 3 parts of dimethylformamide dimethyl acetal with 4 parts of morpholine and heated to 110 °C as by-products were collected by distillation. After about 4 hours, the mixture was heated to 200 °C for about 2 hours as by-products were collected by distillation. The mixture was cooled and solid product was collected from ethyl acetate.

[0099] Example 5

[00100] Bimethylimidazolidene ethylene was prepared by combining 5 parts of N,N'methylethylenediamine (Formula X, where R_1= $-CH_3$, and R_2 = -($CH_2)_2$-) and 6 parts of dimethylformamide dimethyl acetal and heating the solution to about 150 °C for about 4 hours during which time, by-products are collected by distillation. The resulting mixture was cooled and distilled to give 4 parts of product. Product was luminescent on exposure to air.

[00101] Example 6

[00102] Bis(1,3-diphenylimidazolidine) (Formula X, where R_1 = $-C_6H_5$, and R_2 = -($CH_2)_2$-) was prepared by combining 1 part of N,N'-diphenylethylenediamine and 5 parts of triethyl orthoformate and heating the solution to about 200 °C for about 4 hours during which time, by-products are collected by distillation. The resulting mixture was cooled, filtered and washed with ether to give 1 part of product. Product was luminescent on exposure to air.

[00103] Example 7

[00104] 2,2'-Ethylene- 1,1'-biisoquinolylidene (VII) can be prepared as described by Maeda, et. al. in J. Chem. Soc. Perkin Trans 2, 1996, p.121-126 by heating 1,1'-biisoqunoline with 1,2-dibromoethane for 4 hrs. Salt of the product is isolated by filtering, washing with dimethylformaldehyde (DMF) and recrystallizing with methanol. An aqueous solution of the salt is treated with is treated with excess $Na_2S_2O_4$ and Na_2CO_3 and extracted with chloroform to give product. When exposed to air the solution will be luminescent.

[00105] Example 8

[00106] 2-Aminopyridine Schiff base (Formula VIII, where R_1, and R_2 = $-CH_3$) can be prepared as described by Channon, et. al. in Chemical Communications, 1969, p92-93 by heating 2aminopyridine and isobutyraldehyde in toluene with p-toluene sulfonic acid as catalyst. The product will be luminescent on exposure to air, dimethyl sulfoxide, and potassium t-butoxide.

[00107] Examples of Fill Mixtures

[00108] Example 9

[00109] Tetrakis(dimethylamino)ethylene (Formula X, where R_1 and R_2 = $-CH_3$), 1 part, and heavy mineral oil, 9 parts, were combined under an argon atmosphere. The resulting mixture luminesced brightly on exposure to air.

[00110] Example 10

[00111] Tetrakis(dimethylamino)ethylene(Formula X, where R_1 and R_2 = $-CH_3$), 1 part, and polyethylene glycol, 9 parts, were combined under an argon atmosphere. The resulting mixture luminesced brightly on exposure to air.

[00112] Example 11

[00113] Tetrakis(pyrrolidinyl)ethylene (Formula X, where R_1 and R_2 = $-(CH_2)_4-$), 1 part, and heavy mineral oil were combined, 9 parts, under an argon atmosphere. The resulting mixture luminesced brightly on exposure to air.

[00114] Example 12

[00115] Tetrakis(pyrrolidinyl)ethylene (Formula X, where R_1 and R_2 = -($CH_2)_4$-), 1 part, and polyethylene glycol, 9 parts, were combined under an argon atmosphere. The resulting mixture luminesced brightly on exposure to air.

[00116] Example 13

[00117] Tetrakis(pyrrolidinyl)ethylene (Formula X, where R_1 and R_2 = -($CH_2)_4$-), 1 part, and silicone oil, 9 parts, were combined under an argon atmosphere. The resulting mixture luminesced brightly on exposure to air.

[00118] Example 14

[00119] Tetrakis(dimethylamino)ethylene(Formula X, where R_1 and R_2 = -CH_3), 1 part, heavy mineral oil, 7 parts, and titanium dioxide, 2 parts, were combined under an argon atmosphere. The resulting mixture luminesced brightly on exposure to air.

[00120] Example 15

[00121] Tetrakis(dimethylamino)ethylene(Formula X, where R_1 and R_2 = -CH_3), 1 part, light mineral oil, 7 parts, and titanium dioxide, 2 parts, were combined under an argon atmosphere. The resulting mixture luminesced brightly on exposure to air.

[00122] Example 16

[00123] Tetrakis(dimethylamino)ethylene(Formula X, where R_1 and R_2 = -CH_3), 1 part, heavy mineral oil, 5 parts, polyethylene glycol, 2 parts, and titanium dioxide, 2 parts, were combined under an argon atmosphere. The resulting mixture luminesced brightly on exposure to air.

[00124] Example 17

[00125] Tetrakis(pyrrolidinyl)ethylene (Formula X, where R_1, and R_2 = -($CH_2)_4$-), 1 part, heavy mineral oil, 5 parts, polyethylene glycol, 2 parts, and titanium dioxide, 2 parts, were combined under an argon atmosphere. The resulting mixture luminesced brightly on exposure to air.

[00126] Example 18

[00127] Heavy mineral oil, 69 parts, thickener (paraffin wax), 6 parts, and activator (1-octanol), 0.5 parts, were combined and heated enough to create a solution. This was allowed to stand overnight. To this mixture, titanium dioxide, 15 parts, and tetrakis(pyrrolidinyl)ethylene (Formula X, where R_1 and R_2 = -($CH_2)_4$-), 10 parts, were added under an argon atmosphere. The resulting thick paint-like mixture luminesced brightly on exposure to air.

[00128] Example 19

[00129] Heavy mineral oil, 59 parts, thickener (paraffin wax), 6 parts, surfactant (Rhodasurf DA-630), 10 parts, and activator (1-octanol), 0.5 parts, were combined and heated enough to create a solution. This was allowed to stand overnight. To this mixture, titanium dioxide, 15 parts, and tetrakis(pyrrolidinyl)ethylene (Formula X, where R_1 and R_2 = - $(CH_2)_4$-), 10 parts, were added under an argon atmosphere. The resulting thick paint-like mixture luminesced brightly on exposure to air.

[00130] Example 20

[00131] Polyethylene glycol, 58 parts, heavy mineral oil, 5 parts, surfactant (2-(2-octadecyloxyethoxy)ethanol), 3 parts, thickener 1 (paraffin wax), 3 parts, and thickener 2 (poly(ethylene glycol)distearate), 3 parts, were combined and heated enough to create a solution. The resulting solution was allowed to cool to room temperature and stand overnight. To this, titanium dioxide, 20 parts, and thickener, 3 parts, were added. This was again allowed to stand overnight. To this mixture, tetrakis(dimethylamino)ethylene (Formula X,

where R_1 and R_2 = $-CH_3$), 4 parts, was added under an argon atmosphere. The resulting thick paint-like mixture luminesced brightly on exposure to air.

[00132] Example 21

[00133] Heavy mineral oil, 37 parts, surfactant ((octadecyloxyethoxy)ethanol), 5 parts, thickener 1 (paraffin wax), 4 parts, thickener 2 (soluble starch), 5 parts, thickener 3 (poly(ethyleneglycol)distearate), 2 parts, activator 1 (t-butanol), 2 parts, and activator 2 (1,3-butanediol), 2 parts, were combined and heated enough to create a solution. This was allowed to stand overnight. To this mixture, titanium dioxide, 15 parts, zinc sulfide, 5 parts, and tetrakis(dimethylamino)ethylene (Formula X, where R_1 and R_2 = $-CH_3$), 2 parts, were added under an argon atmosphere. The resulting thick paint-like mixture luminesced brightly on exposure to air.

[00134] Example 22

[00135] Heavy mineral oil, 54 parts, thickener (paraffin wax), 6 parts, surfactant (Rhodasurf DA-630), 10 parts, and activator (1-octanol), 0.5 parts, were combined and heated enough to create a solution. This was allowed to stand overnight. To this mixture, titanium dioxide, 15 parts, fumed silica, 5 parts, and tetrakis(pyrrolidmyl)ethylene (Formula X, where R_1 and R_2 = $-(CH_2)_4-$), 10 parts, were added under an argon atmosphere. The resulting thick paint-like mixture luminesced brightly on exposure to air.

[00136] Example 23

[00137] Heavy mineral oil, 76.5 parts, thickener (virgin paraffin wax), 3.5 parts, and activator (1-octanol), 1 part, were combined and heated enough to create a solution. This solution was allowed to stand overnight. To this mixture, titanium dioxide, 11 parts, and tetrakis(pyrrolidinyl)ethylene (Formula X, where R_1 and R_2 = $-(CH_2)_4-$), 8 parts, were added under an argon atmosphere. The resulting thick paint-like mixture luminesced brightly on exposure to air.

[00138] Examples of Projectiles

[00139] The gelatin shell materials in the examples below were prepared using a melt containing gelatin (43-60%), water (30-35%), glycerin (5-10%), sorbitol (5-10%), and dye (<2%).

[00140] Example 24

[00141] Fill mixture was prepared as in Example 12 and encapsulated into a thin spherical gelatin shell. The resulting projectile was fired from a paint ball gun and luminesced brightly when crushed.

[00142] Example 25

[00143] Fill mixture was prepared as in Example 18 and encapsulated into a thin spherical gelatin shell. The resulting projectile was fired from a paint ball gun and luminesced brightly when crushed.

[00144] Example 26

[00145] Fill mixture was prepared as in Example 19 and encapsulated into a thin spherical gelatin shell. The resulting projectile was fired from a paint ball gun and luminesced brightly when crushed.

[00146] Example 27

[00147] Fill mixture was prepared as in Example 20 and encapsulated into a thin spherical gelatin shell. The resulting projectile was fired from a paint ball gun and luminesced brightly when crushed.

[00148] Example 28

[00149] Fill mixture was prepared as in Example 21 and encapsulated into a thin spherical gelatin shell. The resulting projectile was fired from a paint ball gun and luminesced brightly when crushed.

[00150] Example 29

[00151] Fill mixture was prepared as in Example 22 and encapsulated into a thin spherical gelatin shell. The resulting projectile was fired from a paint ball gun and luminesced brightly when crushed.

[00152] Example 30

[00153] Fill mixture was prepared as in Example 23 and encapsulated into a thin spherical gelatin shell. The resulting projectile was fired from a paint ball gun and luminesced brightly when crushed.

[00154] While the compounds have been described and illustrated in conjunction with a number of specific configurations, those skilled in the art will appreciate that variations and modifications may be made without departing from the principles herein illustrated, described, and claimed. The present invention, as defined by the appended claims, may be embodied in other specific forms without departing from its spirit or essential characteristics. The compounds described herein are to be considered in all respects as only illustrative, and not restrictive. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

CLAIMS

What is claimed is:

1. A luminescent projectile comprising;

a fill material comprising [or including],

an autoxidative luminescent substrate capable of luminescent quantum yields in the range of 1 to 0.00001, preferably 1 to 0.001 Einsteins per mole;

a carrier comprising a solvent that allows dissolution and or dispersion of the luminescent agent

a thickening agent

a pigment.

a capsule containing the autoxidative luminescent substrate.

2. A luminescent projectile as in Claim 1 wherein the autoxidative luminescent substrate is one or more of the compounds selected from the group: benzothiazoles, 2,4,5-triarylimidazoles, indoles, N-substituted acridan nitriles and carboxylate esters, biacridene, 1,1'bisisoquinolimum quaternary salts, products of 1,1 'bisisoquinolinium quaternary salts reaction with base, 2aminopyridine Schiff bases, inidazo[1,2-a]pyridine-3(2H)-ones, and tetrakis(dialkylamino)ethylenes.

3. A luminescent projectile as in Claim 1 wherein the carrier additionally comprises one or more of diluents, carriers, solvents, catalysts, thickeners, enhancers, preservatives, stabilizers, surfactants and additives to give a suitable target marking composition.

4. A luminescent projectile as in Claim 3 wherein the solvent is one or more of mineral oil, polyethylene glycol, silicone oil, or vegetable oil.

5. A luminescent projectile as in Claim 3 wherein the thickening agent is one or more of candelilla wax, paraffin wax, virgin paraffin wax, petrolatum, or polysorbitol.

6. A luminescent projectile as in Claim 3 wherein the pigment is one or more of alumina, barium oxide, iron oxide, silica, titanium dioxide, zinc oxide.

7. A method for manufacturing a luminescent projectile comprising:

encapsulating in a paint-ball suitable casing a fill material comprising:

an autoxidative luminescent substrate capable of luminescent quantum yields in the range of 1 to 0.00001, preferably 1 to 0.001 Einsteins per mole;

a carrier comprising a solvent that allows dissolution and or dispersion of the luminescent agent

a thickening agent

a pigment.

8. A method of marking an object with a chemiluminescent material comprising: impacting the object with a projectile that breaks on impact releasing an autoxidative luminescent substrate to expose it to an oxidizer composition to initiate autoxidation., the substrate comprising:

an autoxidative luminescent substrate capable of luminescent quantum yields in the range of 1 to 0.00001, preferably 1 to 0.001 Einsteins per mole;

a carrier comprising a solvent that allows dissolution and or dispersion of the luminescent agent

a thickening agent

a pigment.

9. A method as in claim 6 wherein the oxidizer composition is outside the projectile in the air surrounding the object.

10. A method as is claim 6 wherein the oxidizer composition is contained in the projectile in a compartment reactively separate from the substrate, the compartment constructed such that upon the impact, the oxidizer and the substrate come into contact.

11. A method as in claim 8 wherein the oxidizer composition is air, hydrogen peroxide, alkyl peroxide or aryl peroxide.

12. A luminescent projectile system comprising:

a. An autoxidative luminescent substrate or system such as 1, benzothiazoles, II, 2,4,5-triarylimidazoles, III, indoles, IV, N-substituted acridan nitriles and carboxylate esters, V, biacridene, VI, 1,1'bisisoquinolimum quaternary salts, VII, products of 1,1 'bisisoquinolinium quaternary salts reaction with base, VIII, 2aminopyridine Schiffbases, IX, inidazo[1,2-a]pyridine-3(2H)-ones, and X, tetrakis(dialkylamino)ethylenes capable of luminescent quantum yields in the range of 1 to 0.00001 Einsteins per mole, preferably 1 to 0.001 Einsteins per mole;

b. Combined with auxiliary non-quenching component capable diluents, carriers, solvents, catalysts, thickeners, enhancers, preservatives, stabilizers, surfactants and additives to give a suitable target marking composition, such as mineral oil, polyethylene glycol, silicone oil, vegetable oil, candelilla wax, paraffin wax, petrolatum, polysorbitol, alumina, barium oxide, iron oxide, silica, titanium dioxide, zinc oxide, iso-butanol, t-butanol, ethylene glycol, ethylhexanol, n-octanol, isooctanol, n-decanol, n-hexadecanol, Rhodacal™ reagents, Rhodasurf™ reagents, stearic acid, Tween™ reagents, starch, cellulose, fumed silica, talc, FD&C yellow, blue, or red, Phthalocyanine green, or blue, calcium chloride, calcium sulfate, lithium aluminum hydride, lithium bromide, lithium chloride, magnesium sulfate, sodium borohydride, sodium sulfate, or the like; and,

c. Contained in a protective component compatible capsule of such a composition that the contents do not leak through and the filling is protected from unwanted exposure to oxygen and moisture and suitable for use as a projectile in compressed gas operated guns such as a paint ball marker, such as gelatin, hydrocarbon polymer (such as polyacrylate, polyethylene, polystyrene, polyvinyl alcohol, or the like) diethylene glycol, glucose, glycerin, mineral oil, parabens, starch, polyglycerol, sorbitol, or the like.

[00155] Abstract of the Disclosure

[00156] Chemiluminescent agents in combination with filler materials useful for projectiles are disclosed. Methods for making paint balls useful in low light exercises is also disclosed.

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